

Processes Affecting the Benthic Flux of Trace Metals into the Water Column of San Francisco Bay

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ABSTRACT

Locally regulated point sources represent a significant input of trace metals to San Francisco Bay, especially in the southern component (South Bay) during the dry seasons and periods of drought. However, with recent recognition of the importance of non-point sources, a variety of approaches are being used to evaluate sediment remobilization and subsequent benthic flux of trace contaminants. The extent to which chemical processes couple with diffusive and advective physical processes in regulating benthic flux is also being examined. In terms of metal-speciation controls on solute remobilization and benthic flux, we are investigating the importance of metal-sulfide complexation relative to complexation with dissolved organic substances by determining both metal and ligand fluxes simultaneously. Consistent with previously reported water-column measurements, dissolved pore-water sulfide concentrations, measured at two South Bay sites in July, 1997 and September, 1998, increased with sediment depth from around 10 nM near the sediment-water interface to as high as 980 nM within the top 10 cm, suggesting a source to the water column. Diffusive flux for sulfides estimated from pore-water profiles ranged from 11 to 45 nmoles-m⁻²-h⁻¹. As a complement to the pore-water approach, core-incubation experiments were used to directly measure sulfide benthic flux which ranged from 92 to 480 nmoles-m⁻²-h⁻¹ over the same period. The significant difference between these two approaches was attributable to biologically enhanced advection (bioturbation/irrigation). Although sulfide benthic flux has been found to be consistently positive (that is, out of the sediment as much as 948 nmoles-m⁻²-h⁻¹), benthic fluxes for dissolved organic carbon (0.2 µm filtered, DOC), copper and cadmium are temporally variable in direction across the sediment-water interface, suggesting the importance of DOC complexation in regulating metal benthic flux. Quantifying and understanding processes that affect the variability of these fluxes would enhance water-quality modeling for this estuary.

INTRODUCTION

Although locally regulated point discharges of metals represent a significant source to San Francisco Bay, recent studies have consistently indicated that non-point sources of trace contaminants are also significant (Flegal and others, 1991, Flegal and Sanudo-Wilhelmy, 1993, Wood and others, 1995; Caffrey and others, 1996, Kuwabara and others, 1996). Water-

quality managers have, therefore, been motivated to develop regional monitoring studies to quantitatively describe the fate of these sources in “sources and loadings” models (that is, solute input-output box models) for the estuary. Three approaches have been used in complementary studies, within and outside the USGS, to determine

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benthic fluxes: diffusion gradient calculations based on pore-water profiles, direct flux measurements by core-incubations, and *in-situ* flux chamber experiments. A comparison of values measured by these different approaches can help identify processes that regulate benthic fluxes of toxic substances as well as substances

that affect their chemical speciation, partitioning, and toxicity. This paper provides descriptions of the spatial and temporal variations in benthic flux for trace metals and reactive ligands. Those ligands are represented by dissolved organic carbon, as a model for complexation with natural organics, and dissolved sulfides.

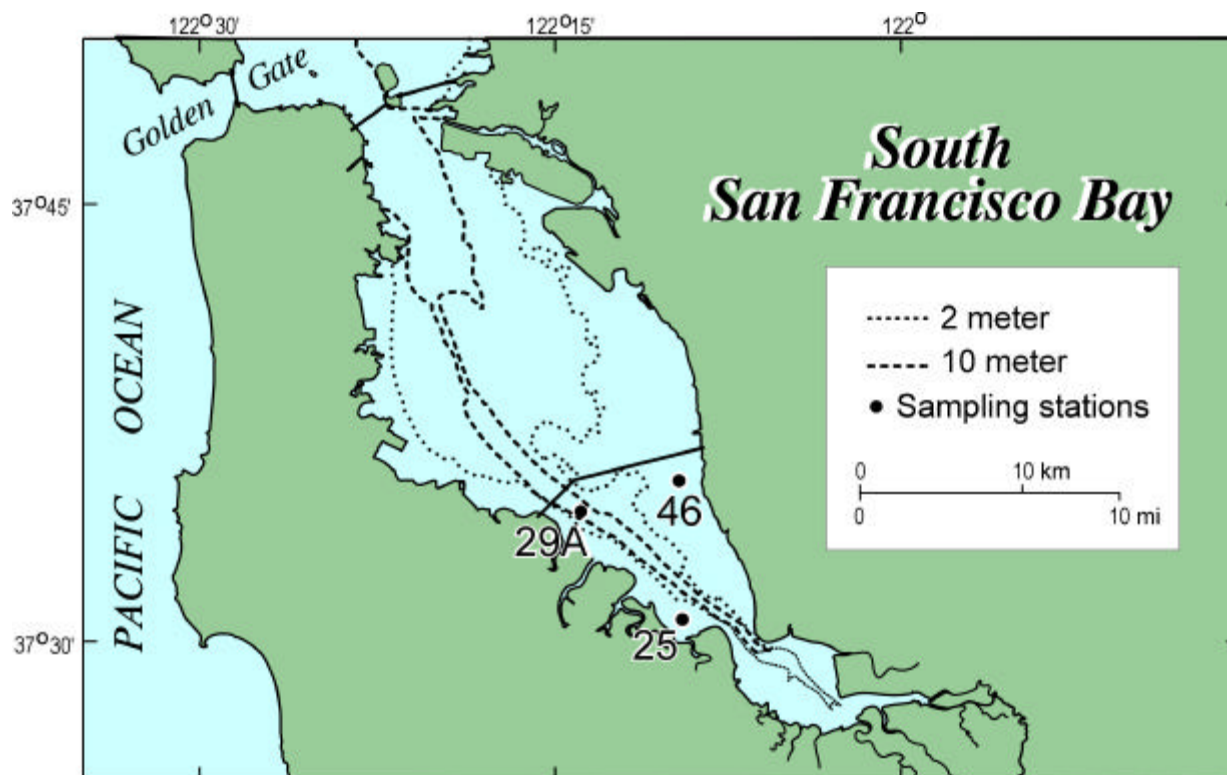


Figure 1. Site map showing three sampling stations in the southern component of San Francisco Bay (South Bay) where benthic flux measurements of trace solutes and nutrients have been made.

METHODS

Three sampling stations in the southern component of San Francisco Bay (South Bay; fig. 1) were used to determine benthic flux for dissolved (0.2 micron filtered) constituents by core-incubation experiments (Caffrey and others, 1996) and by diffusive flux calculations (Kuwabara and others, 1999). One site was located in the main channel (station 29A; approximately 14 m depth), while the other two represented shallow stations (<5 m depth), one on the eastern side of the main channel (station 46), and the other on the western side (station 25).

Dissolved organic carbon (DOC) was measured by low-temperature, persulfate/oxygen/ultraviolet oxidation (Hunter and

Kuwabara, 1994) and by high-temperature non-catalytic oxidation (Qian and Mopper, 1996) within one day of sampling. Dissolved sulfide concentrations were determined by square-wave voltammetry (Kuwabara and Luther, 1993) typically within two hours of sampling. Samples for trace metal analysis were filtered, acidified (pH 2) and stored in darkness at 3°C. Trace-element concentrations were determined by atomic absorption spectroscopy (Kuwabara and others, 1996) and by flow-injection inductively-coupled plasma mass spectrometry (Topping and Kuwabara, 1999).

RESULTS AND DISCUSSION

Processes that control the biological availability of trace inorganic solutes in the oxic water column of South San Francisco Bay have been investigated (Kuwabara and others, 1989; Donat and others 1994; Kuwabara and others, 1996). Previous water-column studies have suggested the importance of competitive complexation reactions involving dissolved sulfides and dissolved organic substances (Kuwabara and Luther, 1993). Concentrations of certain dissolved metals (e.g., copper and zinc) correlate with concentrations of

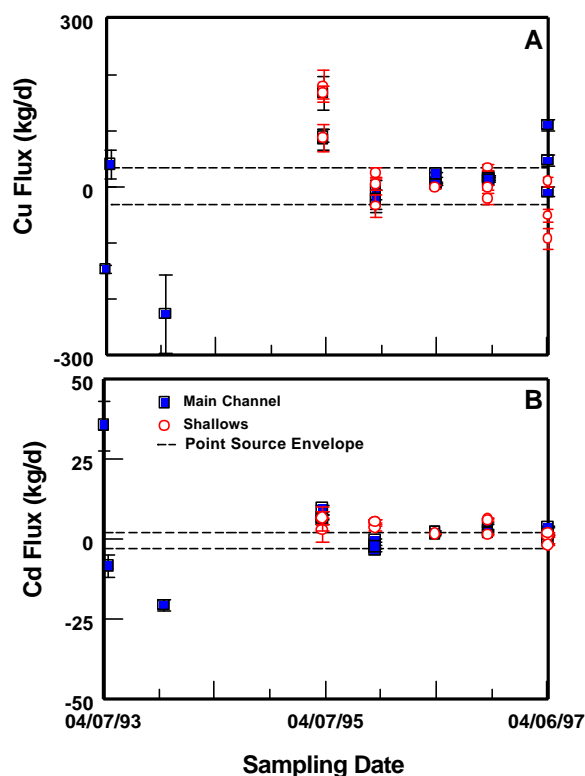


Figure 2. Benthic flux of dissolved copper (Cu; plate A) and cadmium (Cd; plate B) at main channel station 29A and eastern shallow station 46. Dashed lines represent the magnitudes of regulated point sources into the South Bay.

dissolved organic substances in San Francisco Bay (Kuwabara and others, 1989). Dissolved sulfide typically is more concentrated at depth, suggesting a primary benthic source, and no longitudinal sulfide gradients or water column sources have been observed. In contrast, longitudinal gradients for dissolved organic carbon (DOC) have been routinely observed in the estuary due to freshwater sources of natural organic material (Kuwabara and

Luther, 1993). Furthermore, vertical gradients for DOC were observed only during periods of salinity stratification. Because the presence of metastable dissolved-sulfide species in the Bay could affect trace metal speciation over ecologically significant concentration ranges (Kuwabara and Luther, 1993), one might therefore expect that the benthic flux of metals, like the flux for dissolved sulfides, would be consistently positive (that is, out of the sediment). However, unlike benthic flux for dissolved sulfide, benthic fluxes for DOC, dissolved copper, and cadmium are temporally variable in direction across the sediment-water interface, suggesting the importance of DOC complexation in regulating metal benthic flux. Note in Figure 2, that the direction of the trace metal fluxes is not always positive as some previous transport models would suggest (Wood and others, 1995). It should also be noted that for both copper and cadmium, the magnitudes of these fluxes are significant relative to regulated point sources. However, because of intra-annual direction shifts, it is not clear how the net flux over annual time scales or longer would compare to point-source inputs to the South Bay.

Concordant with previous water-column studies, experiments using incubation cores and *in-situ* benthic flux chambers indicate consistent sulfide flux out of the sediment. This flux is generated by redox gradients depicted in pore-water profiles for dissolved sulfide (fig. 3). Diffusive flux calculations, based on these pore-water profiles, suggest a benthic sulfide flux of 11 to 45 $\text{nmoles-m}^{-2}\text{-h}^{-1}$, with consistently steeper concentration gradients at western shallow station 25 than at eastern shallow station 46 (fig. 3). Station 25 is characterized by clay and silt bottom sediment, in contrast to unconsolidated sandy sediment at station 46. A comparison of sulfide flux determined directly in core-incubation studies and those calculated from pore-water gradients indicate orders-of-magnitude underestimation by diffusive flux calculations (fig. 4A). This suggests the importance of biologically enhanced advection (bioturbation/irrigation). We are also compelled to examine microbial and macroinvertebrate benthic processes, because simple geochemical relationships raise some clear inconsistencies. For example, the timing of shifts in benthic flux direction for trace metals is not always consistent with shifts in DOC flux direction (fig. 4B), particularly for cadmium which does not form strong complexes with dissolved organic ligands

compared to other trace metals like copper (Perrin, 1983). Our goal is to quantify and understand processes that affect the variability of trace-contaminant benthic fluxes, and thereby improve

water-quality modeling for this estuary. Even with recent additional interest in benthic flux studies, this remains a formidable challenge.

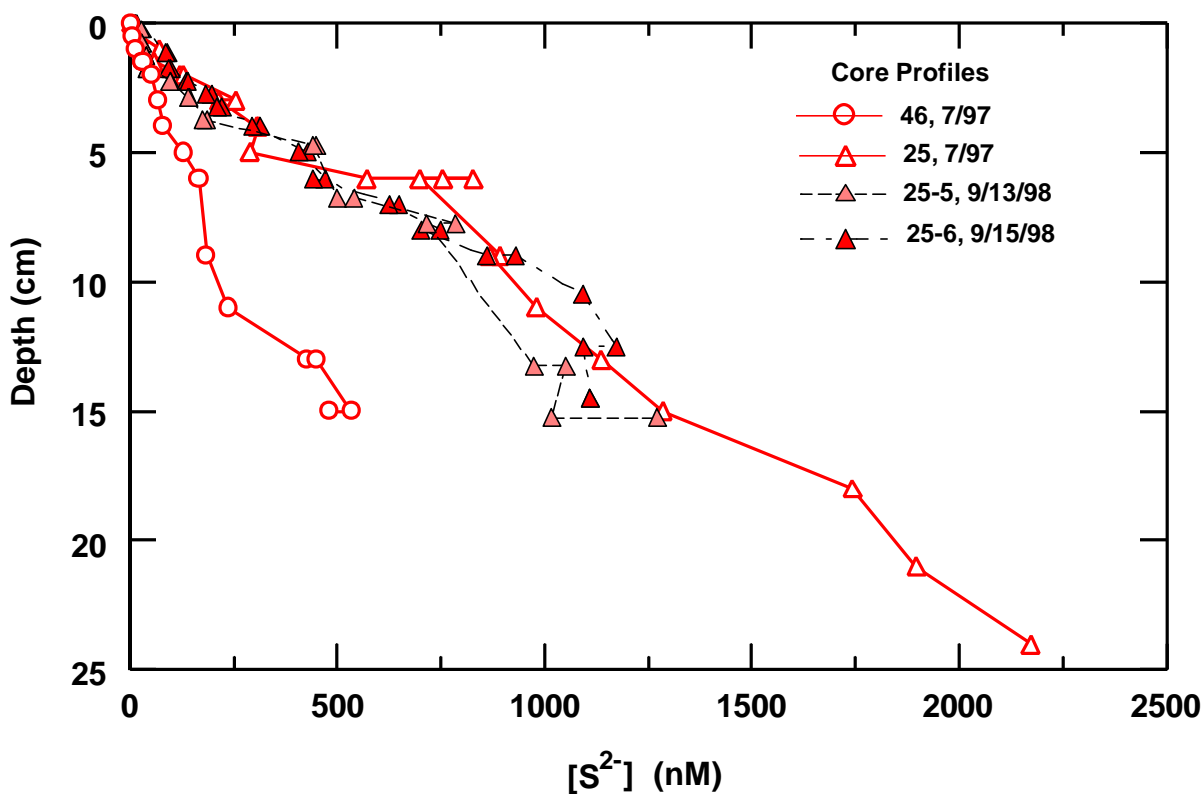


Figure 3. Initial pore-water profiles for dissolved sulfides from cores taken at eastern shallow station 46, and western shallow station 25. Cores 25-5 and 25-6 were replicate cores taken two days apart in September, 1998.

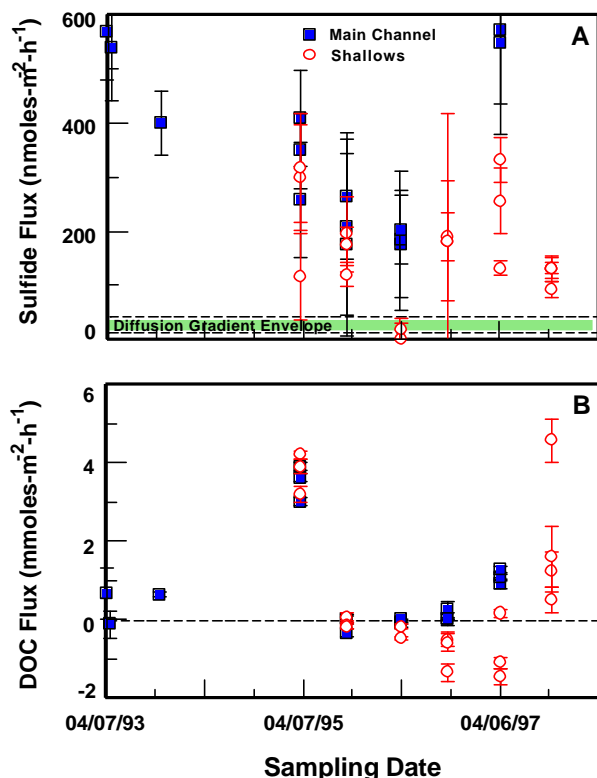


Figure 4. Benthic flux of dissolved sulfides (plate A) and dissolved organic carbon (DOC; plate B) directly measured from core-incubation studies. The diffusion gradient envelope depicted in plate A results from pore-water gradients shown in Figure 3.

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REFERENCES

- Caffrey, J., Hammond, D., Kuwabara, J., Miller, L., and Twilley, R., 1996, Benthic processes in San Francisco Bay: the role of organic inputs and bioturbation, Hollibaugh, J.T., ed., San Francisco Bay: the Ecosystem: American Association for the Advancement of Science, Pacific Division, San Francisco, p. 425-442.
- Donat, J.R., Lao, K.A., and Bruland, K.W., 1994, Speciation of dissolved copper and nickel in South San Francisco Bay: a multi-method approach: *Analytica Chimica Acta*, v. 284, p. 547-571.
- Flegal, A.R., Smith, G.J., Gill, G.A., Sanudo-Wilhelmy, S., Scelfo, G., and Anderson, L.C.D., 1991, Dissolved trace element cycles in the San Francisco Bay estuary: *Marine Chemistry*, v. 36, p. 329-363.
- Flegal, A.R. and Sanudo-Wilhelmy, S., 1993, Comparable levels of trace metal contamination in two semiencloded embayments: San Diego Bay and South San Francisco Bay: *Environmental Science and Technology*, v. 27, p. 1934-1936.
- Hunter, Y.R. and Kuwabara, J.S., 1994, Ionic strength and DOC determinations from various freshwater sources to the San Francisco Bay: *Bulletin of Environmental Contamination and Toxicology*, v. 52, p. 311-318.
- Kuwabara, J.S., Chang, C.C.Y., Cloern, J.E., Fries, T.L., Davis, J.A., and Luoma, S.N., 1989, Trace metal associations in the water column of South San Francisco Bay, California: *Estuarine Coastal and Shelf Science*, v. 26, p. 307-325.
- Kuwabara, J.S. and Luther, G.W., III, 1993, Dissolved sulfides in the oxic water column of San Francisco Bay, California: *Estuaries*, v. 16, p. 567-573.
- Kuwabara, J.S., Chang, C.C.Y., Khechfe, A.I., and Hunter, Y.R., 1996, Implications of dissolved sulfides and organic substances for the chemical speciation of trace contaminants in the water column of San Francisco Bay, California, Hollibaugh, J.T., ed., San Francisco Bay: the Ecosystem: American Association for the Advancement of Science, Pacific Division, San Francisco, p. 157-172.
- Kuwabara, J.S., van Geen, A., McCorkle, D.C., and Bernhard, J.M., 1999, Dissolved sulfide distributions in the water column and sediment pore waters of the Santa Barbara Basin: *Geochimica et Cosmochimica Acta*, in press.
- Perrin, D.D., 1983, Stability Constants of Metal-ion Complexes, Part B: Organic Ligands: Pergamon Press, Oxford, 1263 p.

- Qian, J. and Mopper, K., 1996, Automated high-performance, high-temperature combustion total organic carbon analyzer: Analytical Chemistry, v. 68, p. 3090-3097.
- Topping, B.R. and Kuwabara, J.S., 1999, Flow-injection-ICP-MS method applied to benthic flux studies of San Francisco Bay, Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999--Volume 2--Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, this volume.
- Wood, T.M., Baptista, A.M., Kuwabara, J.S., and Flegal, A.R., 1995, Diagnostic modeling of trace metal partitioning in south San Francisco Bay: Limnology and Oceanography, v. 40, p. 345-358.

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